High-temperature defect spectroscopy in ionic crystals

Z H Xie†, M E Smith†, J H Strange† and C Jaeger‡

† Physics Laboratory, University of Kent, Canterbury, Kent CT2 7NR, UK
‡ Max Planck Institut für Polymerforschung, Postfach 3148, D-55021, Mainz, Germany

Abstract. The first direct NMR spectroscopic evidence of defects in crystalline Li_2O powders containing aliovalent impurities is reported. Quadrupole-perturbed ^7Li satellite transitions are seen above 600 K, which clearly arise from interaction of lithium defects. At about 900 K structure in the satellite transitions indicates two distinct quadrupolar interactions. The relative intensity of the satellites decreases with increasing temperature, which is interpreted as thermal dissociation of an impurity–vacancy complex.

1. Introduction

Point defects in ionic crystals are of considerable interest since they are responsible for the electrical conductivity in simple solids [1]. Study of ionic and defect mobility is of considerable importance for understanding the dynamical properties, and a number of methods, such as ionic conductivity, tracer diffusion, plastic deformation, neutron scattering and NMR, have been used (see [2] for a review). NMR relaxation has clearly demonstrated itself to be a powerful method for examining microscopic motion in cases where suitable probe nuclei exist. ^7Li is a perfect probe nucleus with high NMR sensitivity and it has many applications in technologically useful solid electrolytes. Relaxation work is complemented by spectroscopy that reveals structural information and can provide direct information about the size of the interactions present.

Both NMR relaxation and spectra depend on the nature of the interactions experienced by the nucleus. In diamagnetic insulating solids three principal interactions perturb NMR spectra, namely chemical shift, dipolar and for nuclei with spin numbers (I) greater than $\frac{1}{2}$ electric quadrupole interactions. For ^7Li ($I = \frac{3}{2}$) it has an extremely small chemical shift interaction so that only the dipolar interaction, coupling to other nuclei magnetic moments, and quadrupolar interaction, coupling between the nuclear quadrupole moment (eQ) and a gradient in the electric field (EFG, with a maximum component of eq) set up by an asymmetric distribution of external charges in the neighbourhood of the nucleus, are important. It is convenient to characterize the quadrupole interaction in terms of a coupling constant $C_Q (= e^2 q Q / h)$ and asymmetry parameter η [3]. This quadrupolar interaction provides a microscopic view of defects. The effect of the defects on the NMR signal via the quadrupole interaction will be twofold: (i) loss of the local symmetry, causing an EFG at the nucleus, giving rise to a lineshape and (ii) the mobile defects, giving rise to a time-dependent interaction that causes relaxation.

The presence of defects and their effect on lineshape has been extensively summarized [4]. Several known examples exist, including point defects created in alloys that cause a loss of signal intensity as there is production of a substantial field gradient as defects are

introduced, so only the central $(\frac{1}{2} \leftrightarrow -\frac{1}{2})$ transition is observable, as the outer transitions, which are perturbed by the quadrupole interaction to first order, are 'wiped out' or lost from the spectrum [5]. One of the common ways of setting the magic angle was via the bromine resonance of KBr, which involves looking for the set of narrowest sidebands for the non-central transitions, which in this cubic crystal lattice must result from defects in the structure [6], and similar observations have been made for AgBr [7]. In indium-substituted GaAs electric field gradients are set up by the strain fields around the substitutional indium atoms and the perturbed NMR spectra were used to monitor the distribution of indium atoms within the lattice [8].

Li$_2$O is a fast-ion conductor in its own right and so provides a suitable simple model system for trying to understand relaxation mechanisms prior to examining more complex glassy systems, of which Li$_2$O is an important constituent (e.g. Li$_2$O–SiO$_2$). In Li$_2$O the diffusion constant of Li$^+$ is much higher than that of O^{2-} [9]. The lithium ions sit on a simple cubic sublattice within the antifluorite structure. At high temperature vacancies form from thermally produced intrinsic defects whereas enhanced diffusion at lower temperature can be encouraged by generating additional intrinsic defects by doping small amounts of materials with differing charges into the structure. Here 0.2 mol% LiF was added, which creates vacancies on 0.1% of the lithium sites. NMR relaxation can be used to monitor the concentration and migration of vacancies in the structure. Previously extensive NMR relaxation studies have been reported that reveal two T_1 minima, a higher-temperature one from the Li–Li dipolar interaction and a lower-temperature one that results from the quadrupolar interaction of the lithium with the defects [10].

In principle from NMR spectra the different interaction strengths could be obtained. If any structure can be observed in the lineshape this may help to constrain the interactions. A combination of NMR at high temperatures to produce some motional narrowing and room-temperature magic angle spinning produce lineshapes from which a quadrupole interaction can be deduced. It is shown that one of the defects present produces a well defined quadrupole interaction even when motional narrowing is advanced and that the number of vacancy–impurity complexes decreases with temperature, as expected for thermal dissociation of a paired defect structure.

2. Experimental details

Two Li$_2$O samples were prepared, one nominally pure and the other doped with 0.2 mol% LiF. The samples were pre-annealed in a graphite cell at 1200 K, heating and cooling at a rate of 2 °C min^{-1} under a vacuum of 10^{-3} Torr for 12 h. The reacted powders were sealed into a quartz tube under vacuum. Great care was taken to ensure that all traces of moisture were removed to prevent reaction of Li$_2$O with quartz, which is greatly enhanced by the presence of water.

Relaxation times and static NMR spectra were measured from room temperature to 1000 K at a frequency of 19.2 MHz using a Bruker CXP spectrometer and a specially constructed probe. For all spectra a single short pulse (2 μs) that corresponds to a tip angle of about 10° was used, with a sufficient recycle delay to produce full relaxation. Additionally some magic angle spinning spectra were acquired on a Bruker ASX-500 spectrometer operating at 194.37 MHz with a 4 mm double-bearing probe and spinning rates of around 13 kHz. As chemical shifts were not anticipated to vary much for lithium and were not the major interest here all spectra were self-referenced to 0 ppm.
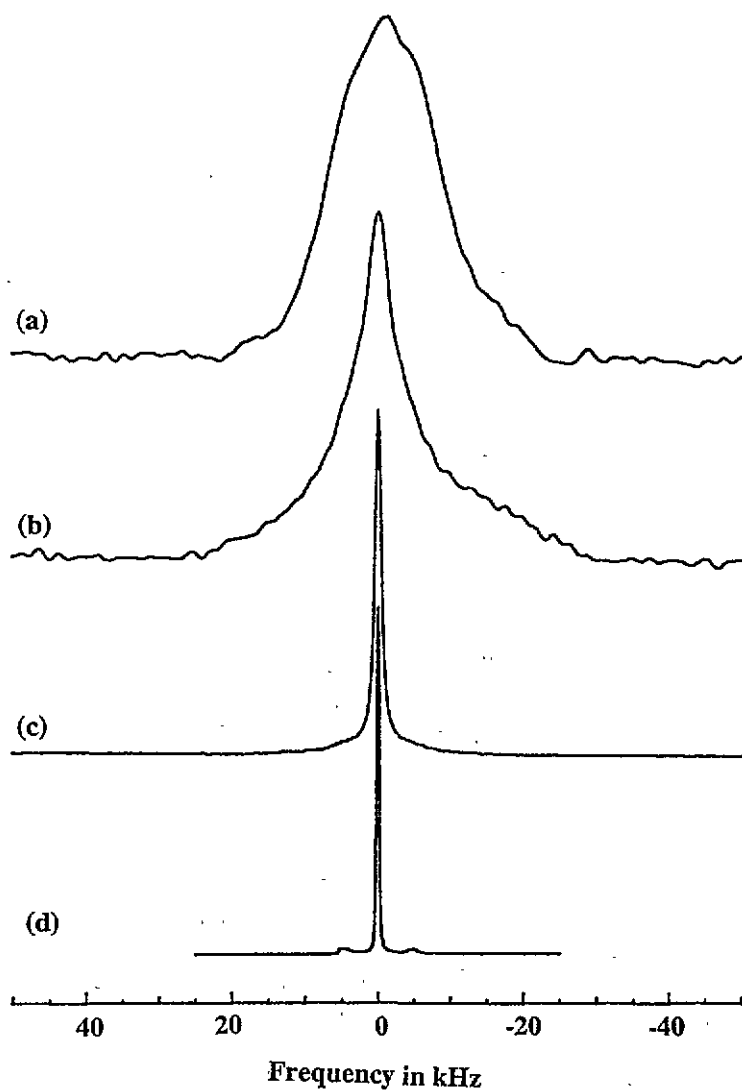
Figure 1. ^{7}Li static NMR spectra from LiF-doped Li_2O at (a) 385 K, (b) 485 K, (c) 535 K and (d) 705 K.

3. Results and discussion

The ^{7}Li static resonance is shown in figure 1 from 385 K to 705 K from an LiF-doped sample. Marked motional narrowing with increasing temperature is apparent from the absorption lineshape. Even at ~ 500 K the line shows a narrower component lying on top of a broadened resonance. The linewidth (FWHM) decreases from around 20 kHz at room temperature to around 300 Hz (for the narrow central component) at 1000 K (figure 2). This behaviour agrees with T_2 measurements [10]. At 705 K (figure 1(d)) the spectrum is dominated by the narrow central component but careful inspection reveals some minor satellite structure. Expansion of the vertical scale reveals at 705 K (figure 3(b)) a well
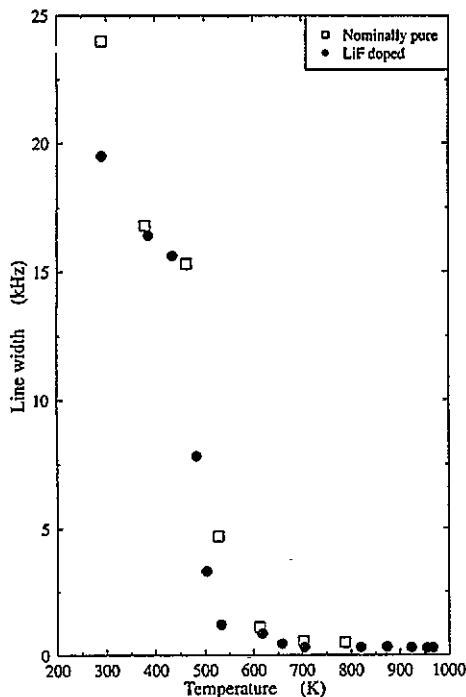
Figure 2. The ^{7}Li static NMR linewidth (FWHM) as a function of temperature for pure and LiF-doped Li$_2$O.

defined, axially symmetric satellite ($\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$) transition powder pattern [3]. Comparison between the pure (figure 3(a)) and doped (figure 3(b)) samples shows that in the pure sample there is very little satellite intensity. Figure 4 shows the development of the satellite structure in the doped sample with temperature. Distinct satellite structure becomes observable at about 620 K with the inner singularities separated by 10 kHz. The spectrum at 705 K (figure 3(b)) shows a classical axial powder pattern ($\eta = 0$) [3]. For the other spectra (figure 4(b)–(d)) the inner singularities and extreme edges of the powder pattern are still well defined although some of the 'broader' intermediate intensity has been lost. Also at 820 K the satellites begin to show some additional structure which becomes resolvable as a clear splitting in the singularities at 875 K and above (figure 4(c) and (d)). Another point in figure 4 is that for each successive spectrum there is a difference in the vertical scale factor of two, indicating that the satellite intensity decreases with temperature. Some magic angle spinning (MAS) spectra were run on the pure and doped samples with fast MAS at room temperature (figure 5). The spectra narrow into a dominant centre band, of identical chemical shift, and a set of side bands. The vertical scale is set so that the extent of the minor side bands can readily be seen, truncating the centre band. The side bands from the doped sample are more intense, hence the better signal to noise from comparable samples, and extend over a wider frequency range.

At room temperature the structure is essentially rigid and the broadening is dominated by the dipolar interaction, which also dominates the relaxation at higher temperatures [10]. The dipolar interaction will be dominated by homonuclear coupling to other lithium ions that sit on a cubic lattice with cell dimension 0.231 nm [11]. The linewidth can be calculated from the second moment [12] using this ionic separation, and assuming a Gaussian lineshape
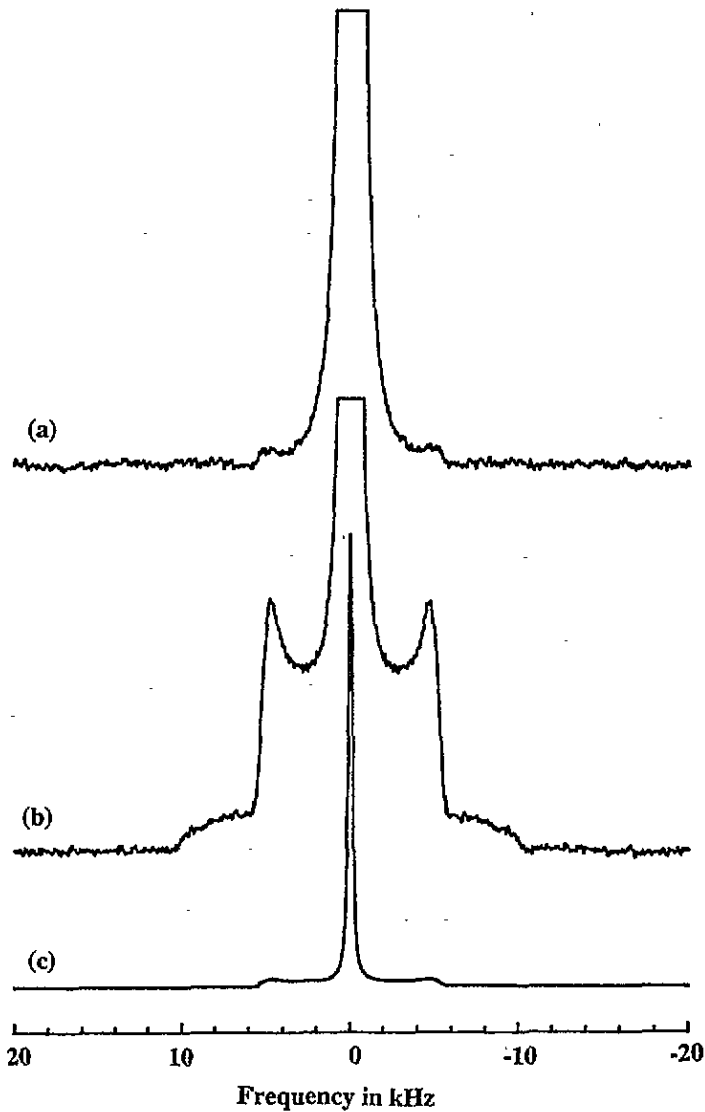
Figure 3. ^{7}Li static NMR spectra at 705 K from (a) pure Li_2O and (b), (c) LiF-doped Li_2O.

produces a linewidth (FWHM) of $\sim$ 20 kHz. This is very close to the value measured, confirming the dipolar dominance of the linewidth. The MAS spectra show that side bands extend over a range ±40 kHz for the pure sample and $> \pm$80 kHz for the doped sample. The fact that the side bands are more intense and extend over a wider frequency range for the doped sample already hints at differences between the samples. The doped sample with its higher concentration of defects means that some subset of the lithiums in the sample will be experiencing a significantly enhanced quadrupolar interaction. In the pure cubic lattice there will be no EFG but the introduction of point defects will result in some sites having a quadrupolar interaction. It is probably the convolution of these two line broadening mechanisms in the doped sample that produces the more intense side bands extending over a significantly larger frequency range than for the pure sample.
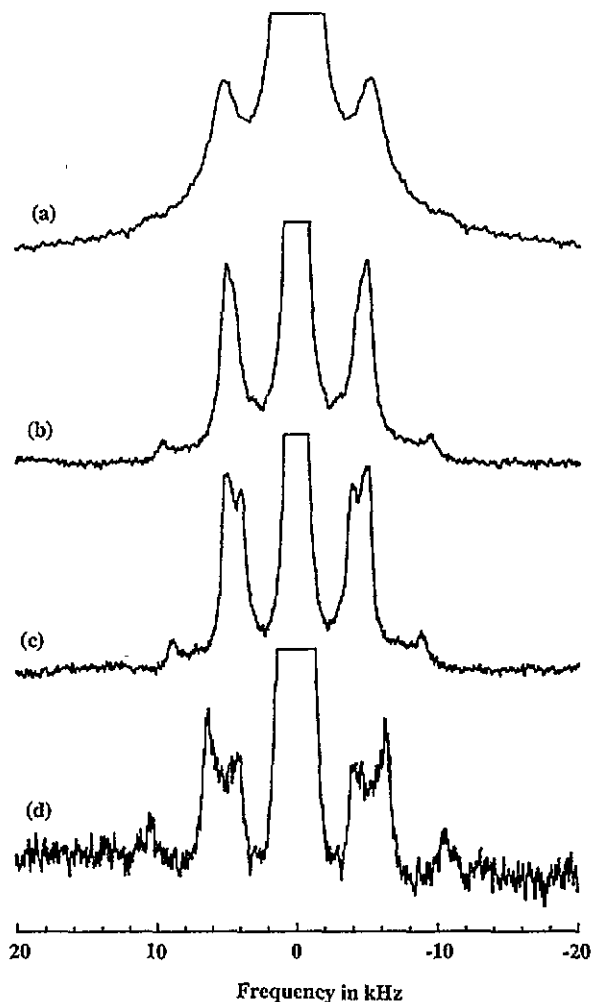
Figure 4. Static ^{7}Li NMR spectra showing the satellite transitions from LiF-doped Li$_2$O at (a) 620 K, (b) 770 K, (c) 875 K and (d) 965 K, with a vertical expansion of a factor of two between each part.

As the temperature is raised and full diffusional motion starts this dipolar interaction begins to be averaged and the linewidth decreases revealing some quadrupolar satellite structure. The separation between the singularities is ν_Q, which for $I = \frac{3}{2}$ is $C_Q/2$. Hence the quadrupolar interaction is $\sim$ 20 kHz. Such a structure could lie under the dipolar-broadened lineshape and it is only when motion averages this away that the more subtle quadrupole structure is revealed. The point that is clear from figure 3 is that this structure can unambiguously be associated with some defect as it is almost entirely absent in the pure sample.

Both quadrupolar and dipolar perturbations to first order vary as $(3\cos^2\theta - 1)$ in axially symmetric situations, where θ is the angle between the largest tensor component and the magnetic field. If both these interactions were from the same source and so were undergoing the same modulation it would be expected that both would be averaged simultaneously.
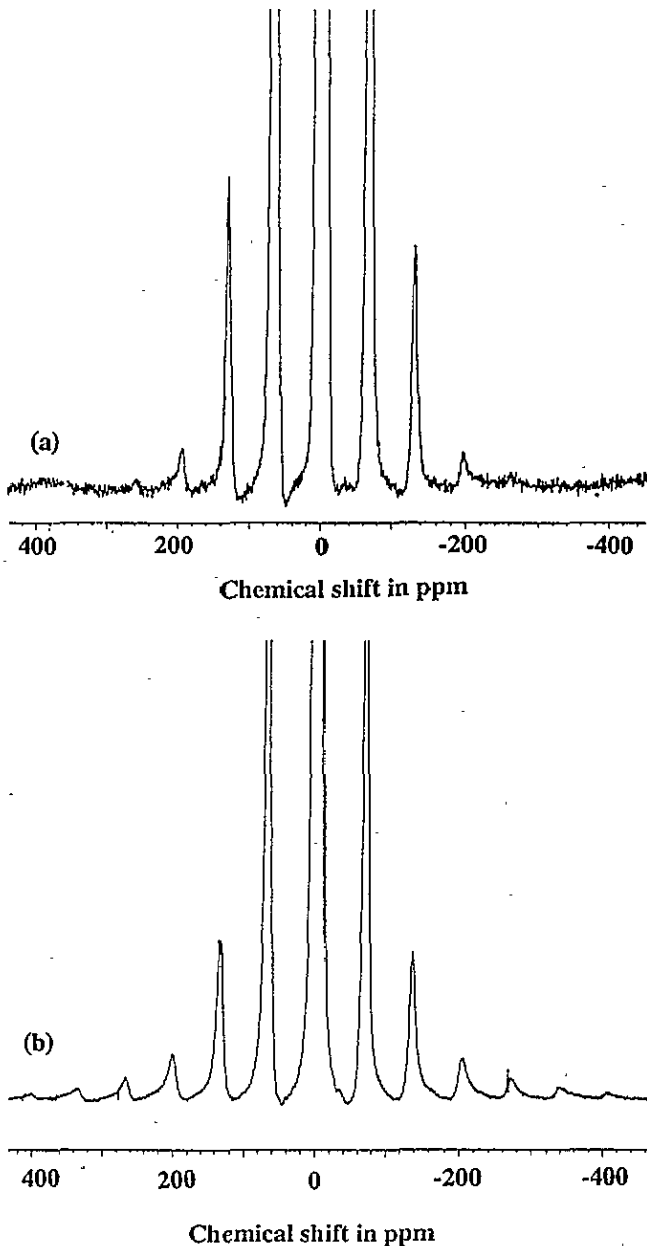
Figure 5. ^7Li MAS NMR spectra at room temperature from (a) pure Li_2O and (b) LiF-doped Li_2O.

Observation of the quadrupolar splitting at higher temperatures presents some interesting questions about the averaging and sources of the interactions since it is apparent that the dipolar interaction is being efficiently averaged while there are parts of the quadrupolar interaction that effectively remain static and impervious to the motion. Hence there is some motion and/or structural unit for which there is effectively some residual average quadrupolar interaction. This differential behaviour of dipolar and quadrupolar interactions implies that their sources and/or averaging processes must be different. Later some possibilities to

explain these observations are suggested. The relaxation data show that the mean time between lithium ion jumps at 700 K is about 3×10^{-8} s. The mean jump time of the vacancies for a vacancy concentration of 2.5×10^{-3} is then 6×10^{-11} s [10]. Using the expressions of Sholl [13, 14] for T_1 the C_Q that results from the T_1 relaxation time of 0.18 s at 1700 K [10] is $\sim$ 200 kHz, and at this temperature there will be a significant dipolar contribution to T_1 that means 200 kHz is likely to be an upper estimate of C_Q. The quadrupolar interaction producing the lineshape is much smaller than the C_Q deduced from relaxation even after the dipolar contribution is considered.

The observation of quadrupolar structure despite fast hopping has been observed in fast-ion conductors with anisotropic structure. For example in sodium β-alumina the sodium is clearly in rapid motion at room temperature from T_1 measurements yet a second-order quadrupolar rotation pattern of the $(\frac{1}{2}, -\frac{1}{2})$ transition corresponding to a C_Q of 1.017 MHz was observed [15]. The situation is somewhat different in sodium β-alumina in that there were no introduced defects and the sodium within a given crystallite hops between sites with the same EFG. In doped Li_2O, because of the presence of fluorine centres, not all lithium sites are equivalent within the structure. Given that the relaxation time measurements confirm that in Li_2O the average jump time of the lithium ions and vacancies is short, some associated or coherent motion must be occurring so part of the quadrupolar interaction does not change at some sites as ions move from site to site. When an F^- replaces an O^{2-} to give local charge balance one of the lithium sites on the unit cell containing the fluorine will be a vacancy. Motion of the vacancy around the lithium sites of this unit cell would cause a large fluctuating EFG at the lithium sites on the adjacent unit cells. The vacancy will be hopping so rapidly that over T_2, each of the corner sites of the cell will be equally occupied by the vacancy. Additionally the presence of the fluorine is a perturbation of the uniformity of the anion sublattice. This will produce a static EFG at the lithium sites on the adjacent unit cells. The average value from the mobile vacancy and the static component from the associated fluorine gives a non-zero average EFG at some lithium sites on neighbouring cells since the EFG is proportional to r^{-3}. There is still a question of the lithium jump motion on the neighbouring unit cell. These jumps would still tend to bring about some averaging of the quadrupole interaction by changing the distance (r) to the defect centre. However, a common feature of many computer simulation models of defects in fluorites is clusters of defects [16]. Even a pair of closely associated fluorine ions (e.g. next-nearest neighbour cells) would result in the lithiums of those unit cells experiencing a non-zero time average part of the quadrupole interaction from the associated group. At this stage we cannot be specific about the type of cluster present but merely point out that any such structure would in principle satisfy the criteria necessary for a non-zero average EFG and hence produce the lineshape observed.

This picture is plausible and would be favoured until the extrinsic vacancies are able to move readily away from the associated fluorine, then the lithiums on the adjacent unit cells will move markedly relative to the fluorine impurity centre. Of course intrinsic vacancies will also be present and allow motion that modulates the lithium–lithium dipolar coupling. However, the static average quadrupolar interaction can persist if the motion is localized around clustered defects as suggested above. Then as the temperature rises the association of the fluorine and the extrinsic vacancy will weaken as thermal energy begins to break them up and dissociation will occur. In fact the loss of intensity in the range above 800 K is expected from the enthalpy of association of lithium vacancies and impurities of 0.6 eV [9]. Once a lithium hops away from a cluster the quadrupolar interaction will begin to be averaged away. This would explain the collapse of the satellite intensity at higher temperatures. The splitting in the satellite pattern implies that two slightly different quadrupolar interactions

must be present, although the source of these is not yet clear. It should be re-emphasized that all the evidence, the absence of quadrupolar satellite structure in the pure sample and the loss of intensity with temperature strongly links the satellites with the impurities, so NMR is directly probing the defect state.

4. Conclusion

The ^{7}Li NMR spectra reported here are clear evidence of a non-zero average quadrupolar interaction between lithium and an impurity centre. The implication is that at lower temperatures some sort of associated motion of the extrinsic defects must be occurring so that at some lithium sites part of the quadrupolar interaction is not averaged away. As the temperature is increased the thermal energy available increases the dissociation of the vacancy–fluorine pairs and results in the quadrupolar interaction being averaged. NMR spectroscopy has been shown to be a good probe of the defect state.

Acknowledgments

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